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Ionomeric membranes based on partially sulfonated poly(styrene): synthesis, proton conduction and methanol permeation

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Abstract

Homogeneuosly sulfonated poly(styrene) (SPS) was prepared with various concentration of sulfonic acid groups in the base polymer. Membranes cast from these materials were investigated in relation to proton conductivity and methanol permeability in the temperature range from 20°C to 60°C. It was found that both these properties increase as the polymer is increasingly sulfonated, with abrupt jumps occurring at a concentration of sulfonic acid groups of about 15 mol%. The most extensively sulfonated membrane exhibited conductivity equal to that of Nafion. As a consequence, this membrane material is potentially an appealing alternative to the very expensive Nafion, for a number of electrochemical applications. For the membrane with the highest degree of sulfonation we measured a methanol permeability about 70% smaller than for Nafion. This characteristic is especially desirable in applications related to the direct methanol fuel cell (DMFC). ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Ionomeric membranes; Sulfonation

1. Introduction

Application of solid polymer electrolyte membranes spans a variety of electrochemical technologies: low-temperature fuel cells, batteries, electrodialyzers, chlor-alkali cells, sensors, electrochromic devices, supercapacitors. Nafion® is a perfluorinated ionomer which has been investigated extensively [1–3], and is largely utilized as a membrane material, particularly in fuel cells and in the chlor-alkali process. At later times, other perfluorinated ionomer membranes, manufactured by Dow Chemical and Asahi, have become commercially available. These materials are structurally analogous to Nafion and have similar properties [4]. While these membrane materials exhibit good chemical stability and proton conductivity, they are very costly. There is an intensive research effort attempting to achieve low-cost nonperfluorinated ionomer membranes to be used in various electrochemical systems. The radiation-grafting technique has been proposed as a valid option to obtain a variety of ion-conducting polymer membranes [5–7]. Some of these membranes are already on the market [8]. Other investigators have formed blends of water-soluble ionomers incorporated into an inert, insoluble polymer matrix and have proposed such membrane materials for use in low-temperature fuel cells [9,10]. Still others have polymerized and cross-linked a monomer

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within an inert membrane matrix and then introduced ionogenic groups into the polymer network [11]. Very recently, the preparation of ceramic membranes doped with several kinds of acids has been reported. These membranes have good mechanical and thermal resistance and very high conductivity [12]. However, it is unclear whether the acid is firmly retained in the membrane for long periods of time or is leached out by the adjacent solution. The preparation of an inorganic–organic network containing sulfonic acid functionalities has been reported [13]. Membranes cast from this material exhibited interesting proton conductivity. Ionomer membranes based on sulfonated polysulfone have also been developed [14,15].

In the present work we have partially sulfonated a commercial noncross-linked poly(styrene) to various extent, obtaining a homogeneous distribution of the sulfonic acid groups in the polymer. Since the resulting materials are not cross-linked, high quality membranes were easily obtained by evaporation-casting from appropriate solvents. The level of sulfonation was carefully adjusted so as to maximize the proton conductivity, while preventing the membrane from becoming soluble in water. Given the stability of the utilized base polymer and the easiness of the preparation procedure, our goal was to attain ionomer membranes having low cost and the potential to be used for some electrochemical applications. In the following account we first describe in detail the synthesis procedure of these membrane materials. We then present results concerning the proton conductivity and the methanol permeability of these membranes. Finally, we discuss potential implications of this work in relation to some electrochemical technologies, particularly the DMFC.

2. Experimental procedures

2.1. Partial sulfonation of poly(styrene)

Our sulfonation procedure is analogous to that described by Weiss et al. [16]. First, acetyl sulfate (the sulfonating reagent) is freshly prepared: a measured amount of acetic anhydride (*Carlo Erba*) is added to 1-2 dichloroethane (DCE, *Carlo Erba*) in a test-tube under a nitrogen atmosphere. The volume of DCE is twice that of anhydride. The solution is cooled to about 0°C, then sulfuric acid (96 wt.%, *Baker*) in stoichiometric amount with respect to the desired virtual degree of sulfonation in the polymer, is added while flowing nitrogen. The molar amount of acetic anhydride is in slight excess with respect to sulfuric acid, so that the latter is completely converted to acetyl sulfate. Finally, the test-tube is capped and the resulting acetyl sulfate in DCE solution is ready to be used.

20 g of atactic poly(styrene) (PS, average molecular weight 52 000) are dissolved in 200 ml of DCE, which has previously been purged with nitrogen in a flask. The flask is capped and the solution, which is maintained under nitrogen throughout the procedure, is then heated to 60°C with reflux condensation. The total amount of the prepared acetyl sulfate solution is syringed through the cap into the flask and the sulfonation reaction is let to proceed for 2 h under stirring. Afterward, the reaction is stopped by adding 10 ml of 2-propanol (*Carlo Erba*). The resulting solution is cooled and concentrated by evaporating about 50 ml of DCE under vacuum. The sulfonated polymer is then precipitated by adding the solution to 1.5 l of distilled water drop by drop by means of a syringe. The polymer is filtered, washed for 2 h in distilled water (about 1 l) at moderate temperature under reflux condensation, and then filtered again. Finally, the polymer is dried under vacuum at 60°C for 2 days.

2.2. Analysis of the sulfonated product

Films of the product were characterized by FT-IR spectroscopy to ascertain the presence of sulfonate groups attached to the phenyl rings. A Perkin-Elmer infra-red spectrometer (model 1600) was used.

The degree of sulfonation in the polymer was evaluated by titration: 0.3 g of the dehydrated sulfonated polymer are dissolved in about 30 ml of a toluene/methanol mixture (9 : 1 vol). A standard 0.1 N solution of sodium hydroxide (Aldrich) in methanol is first diluted five times with methanol and then used to titrate the polymer solution with phenolphthalein as an indicator.

2.3. Preparation of the membranes

A solution (32 g/l) of the sulfonated polymer in a toluene/*n*-butanol mixture (7 : 3 vol) is prepared and

filtered. Part of the solution is poured into a Teflon dish and placed in a vacuum oven at room temperature until complete evaporation of the solvent. Then, the temperature is risen to 50°C and the polymer is vacuum-dried further for 1 h. Finally, the polymer is recovered as a flat-sheet membrane from the bottom of the Teflon dish and soaked in deionized water at 80°C for 3 h, before being tested. The membrane thickness was measured in the dry state by means of a digital micrometer (Heidenhain).

2.4. Conductivity measurements

A four-probes *dc* technique was used to measure the proton conductivity. The in-plane (lateral) conductivities of the membranes were measured by means of a two-compartments test cell. Each compartment was filled with a very dilute solution of sulfuric acid (10^{-5} M, *Carlo Erba*) in deionized water (18 MΩ cm). A detailed description of the cell and experimental setup is presented elsewhere [17]. This technique proved adequate to accurately test membranes with high conductivity [17,18]. For measurements of proton conductivity normal to the plane in membranes with low degree of sulfonation (SPS_{15}), the conventional two-compartments cell configuration, with the membrane arranged orthogonal to the proton current, was also used. Each compartment, equipped with a platinum foil electrode, is filled with concentrated sulfuric acid solution (0.5 M) in deionized water. The two electrodes are connected to an EG & G potentiostat/galvanostat (model 273) working in the galvanostatic mode, and produce a proton current across the membrane. The processes occurring at the electrode surfaces are:

$$\text{Anode}: \quad H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^-$$

$$\text{Cathode}: \quad 2H^+ + 2e^- \rightarrow H_2$$

The applied current intensity was typically of the order of 5 mA, which corresponds to a current density of about 1 mA/cm^2 in the membrane. The ohmic drop across the membrane is measured by means of two electrochemical probes (calomel reference electrodes, Metrohm) — adjacent to each face of the film — connected to a digital multimeter (Keithley, model 2000). The latter experimental setup, though accurate with poorly conductive membranes (low concentration of sulfonate groups in the polymer), proved inadequate with membranes exhibiting conductivity greater than $2 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$, owing to the considerable ohmic drop in the electrolyte solution between each face of the membrane and the adjacent probe. Thus, it could be used successfully only with the SPS_{15} membrane in this work.

2.5. Permeability determinations

The permeability experiments were carried out utilizing a glass diffusion cell. One compartment of the cell ($V_A = 10.2$ ml) was filled with a solution of methanol (8 vol%, Carlo Erba) and 1-butanol (0.2 vol%, Riedel-De Haen) in deionized water. The other ($V_B = 14$ ml) was filled with a 1-butanol (0.2 vol%) solution in deionized water. The membrane (area 4.9 cm^2) was clamped between the two compartments and these were kept under stirring during an experiment. A flux of methanol sets up across the membrane as a result of the concentration difference between the two compartments. A detailed description of the experimental set-up and procedure can be found elsewhere [17]. Under pseudosteady-state conditions, which prevailed during our experiments, and for $c_B \gg c_A$, the methanol concentration in the receiving compartment as a function of time is given by:

$$c_B(t) = \frac{A}{V_B}\frac{DK}{L}c_A(t - t_0) \tag{1}$$

where c is concentration, A and L the membrane area and thickness; D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. The assumptions are made here that D inside the membrane is constant and K does not depend on concentration. The product DK is the membrane permeability. t_0, also termed time lag, is explicitly related to the diffusivity: $t_0 = L^2/6D$ [19].

c_B is measured several times during an experiment and the permeability is calculated from the slope of the straight line. The methanol concentrations were measured by a capillary gas chromatograph (Fison, model 8000) fitted with a flame ionization detector; 1-butanol was used as an internal standard. During permeability and conductivity tests the temperature was controlled by means of a thermostatic water bath. However, lateral conductivity data above room temperature were

collected as the cell was heated up very slowly. The temperature was measured during the latter experiments, by means of a probe located in the cell by one end of the membrane.

3. Results and discussion

The results of our FT-IR analysis indicated clearly the presence of sulfonate groups in the polymer after reaction. We were able to identify the absorbance doublet centered at 1340 cm^{-1} due to the asymmetric stretching vibrations of the S=O bond. The symmetric vibration of this bond produces the characteristic split band of absorbance at $1150 \div 1185\,cm^{-1}$, which we also observed.

We prepared polymers with various degree of sulfonation. That was controlled by reacting the base polymer with different amounts of acetyl sulfate. In this work the virtual sulfonation of the monomeric units was varied between 10% and 20% on a molar basis. In practice, the attained concentration of sulfonate groups in the polymer was somewhat inferior to the one that would correspond to complete conversion of the sulfonating reactant. In Fig. 1 the actual concentration of sulfonic acid groups, as determined by titration, is reported as a function of the concentration calculated on the basis of the utilized amount of acetyl sulfate. It is noted that conversion of the sulfonating reactant is complete for concentration up to 15 mol%. The actual ion-exchange capacities of the sulfonated polymers investigated here are reported in Table 1. The various polymers are denoted in this work by SPS with a suffix indicating the virtual sulfonation degree in moles per cent. We noted that the pliability of the membranes obtained from these materials depends strongly on the sulfonate groups concentration. Our SPS_{10} membranes were rather brittle and stiff as opposed to SPS_{20}, which could be bent extensively, even in the dry state, before brittle rupture occurred. Also, the SPS_{20} films became rather plastic, when hydrated. The films were homogeneous and with a fairly uniform thickness as from Table 1.

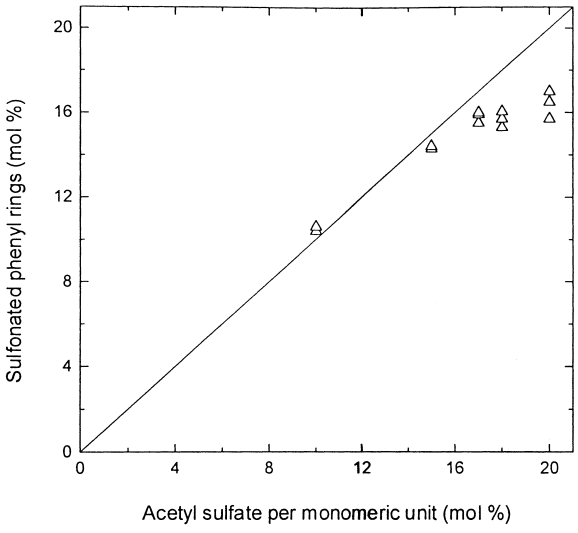

Fig. 1. Degree of sulfonation vs. utilized amount of sulfonating reagent on a monomeric unit base.

3.1. Proton conductivity

Fig. 2 is an Arrhenius plot of the proton conductivity as a function of temperature for the various investigated SPS membranes. Apparently, an Arrhenius-type depencency of conductivity on temperature subsists for all these membranes. The apparent activation energies of proton migration are reported in Table 1 along with the conductivities at room temperature and at 60°C. We note that the activation energy for SPS_{15} is higher than for the more extensively sulfonated membranes; the latter exhibiting activation energy slightly superior to that of Nafion (11 $kJ\,mol^{-1}$). All the data points in Fig. 2 refer to the lateral proton conductivity with the exception of SPS_{15}, for which data indicate the conductivity normal to plane of the membrane. We were able to measure also the lateral conductivity in SPS_{15} at room temperature. As we found essentially no difference between the two conductivity values, we conclude that the membranes were isotropic with regard to proton migration.

While the conductivity of Nafion increases conspicuously as a result of mild thermal treatments, such as soaking in water at moderate temperature (e.g. 80°C) for few hours, SPS membranes turned out quite insensitive to such treatments. Moreover, we observed no degradation of conductivity in SPS membranes soaked in water at room temperature over a 2-months period, as opposed to Nafion, whose conductivity decreased by about 30% over the same period of time [18].

Table 1
Physical properties of the investigated partially sulfonated poly(styrene) membranes

Type	Thickness (μm)	Ion exchange capacity (meq/g)	Conductivity 22°C (Ω^{-1} cm^{-1})	Conductivity 60°C (Ω^{-1} cm^{-1})	Methanol permeability 22°C (cm^2 s^{-1})	Methanol permeability 60°C (cm^2 s^{-1})	E_{act} (proton migration) (kJ mol^{-1})	E_{act} (methanol permeation) (kJ mol^{-1})
SPS_{10}	240	0.93	[a]	[a]	[a]	[a]	–	–
SPS_{15}	105	1.24	1.5×10^{-3}	3.1×10^{-3}	0.27×10^{-7}	0.93×10^{-7}	15.3	26.6
SPS_{17}	233	1.33	2.6×10^{-2}	4.3×10^{-2}	5.2×10^{-7}	13.7×10^{-7}	12.1	17.9
SPS_{18}	196	1.34	3.2×10^{-2}	5.6×10^{-2}	5.2×10^{-7}	10.8×10^{-7}	12.1	17.9
SPS_{20}	338	1.41	5.0×10^{-2}	8.6×10^{-2}	5.2×10^{-7}	11.9×10^{-7}	12.1	17.9

[a] Not measurable.

3.2. Methanol permeability

Fig. 3 shows the concentration of permeated methanol in the diffusion cell as a function of time. The observed linear behavior is in agreement with predictions of Eq. (1). It is important to note that the methanol diffusivity in the least permeable membrane (SPS_{15}) is considerably smaller than in SPS_{17}, as inferred qualitatively from the time lags in Fig. 3. Even the dependency of the permeability upon temperature is of the Arrhenius type, as from Fig. 4. The permeability values at room temperature and at 60°C together with the apparent activation energies of methanol permeation, are also reported in Table 1. Similarly to the behavior observed for proton conduction, the activation energy of methanol permeation in our SPS membranes is very close to that of Nafion membranes (18 kJ mol^{-1}) [18], with the exception of SPS_{15}, for which a considerably higher energy is noted.

3.3. Discussion

In Fig. 5 the membrane conductivity and permeability at room temperature are plotted as a function of the concentration of the sulfonic acid groups in the polymer. As expected, the conductivity rises with increasing concentration. More interesting is the abrupt increase observed at concentration around 15 mol%. That seems indicative of a conductivity percolation threshold. An analogous behavior is noted for the methanol permeability with a sharp jump at the same concentration of sulfonate groups (15 mol%). The simultaneous occurrence of presumed percolation thresholds for conduction and methanol permeation could be understood if these polymers are supposed to have a heterogeneous microstructure with polar ion-rich domains separated from a non-polar dielectric matrix. Such a microphase-separated structure has been observed in Nafion® [20,21] and

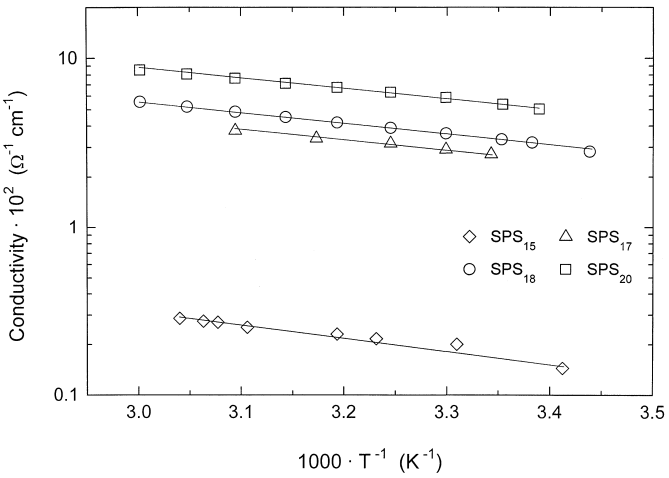

Fig. 2. Arrhenius plot showing the temperature dependency of proton conductivity for the investigated membranes.

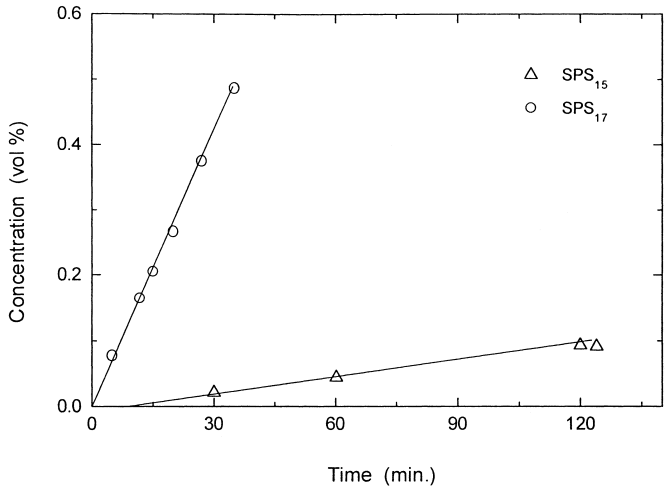

Fig. 3. Concentration vs. time of methanol permeated through two of the investigated membranes.

other noncross-linked ionomers and block copolymer ionomers [22]. It has been proposed that the ion-rich domains are interconnected in Nafion and that ions migrate through these domains, which are also swollen with water. Recently, we provided evidence that a small polar molecule as methanol, also permeates primarily through these hydrophilic regions [17]. If such a picture applies to our sulfonated poly(styrene) as well, then it would be plausible that, at low degree of sulfonation, the ion-rich domains are islands disconnected from one another and long-range conduction or diffusion of methanol cannot occur. As the base polymer is more and more sulfonated, the number and/or the size of these domains increases, so that they eventually become interconnected and a percolation threshold is encountered.

While the membranes are essentially nonconductive below 10 mol% sulfonation, the proton conductivity is quite remarkable at sulfonate concentration above 15 mol%. We measured for SPS_{20} a conductivity of $5 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$ at room temperature, which is very close to the conductivity of Nafion. In principle, a still higher conductivity could be attained, by further sulfonating the polymer; however, we suspect

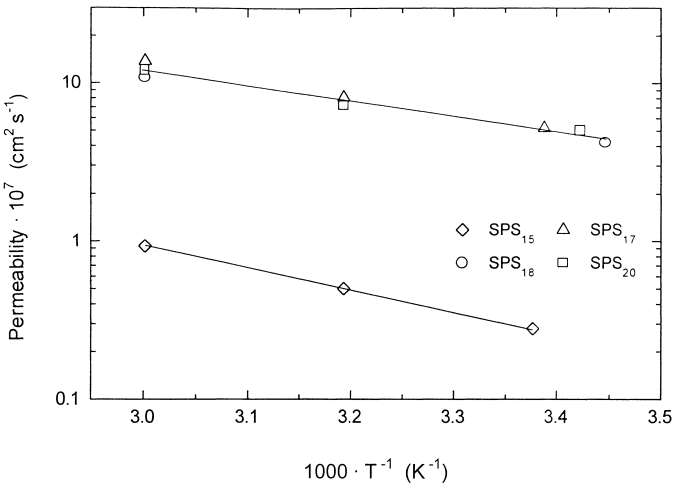

Fig. 4. Arrhenius plot showing the temperature dependency of methanol permeability for the investigated membranes.

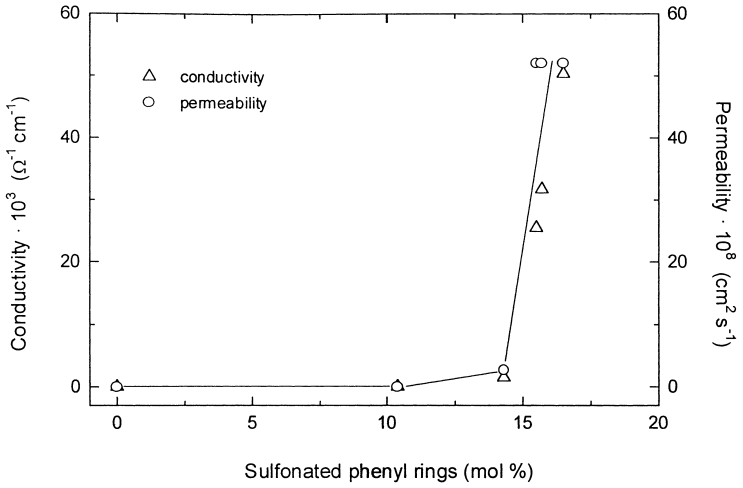

Fig. 5. Proton conductivity and methanol permeability at 22°C vs. concentration of sulfonic acid groups in the polymer.

that the material would then become water-soluble. Generally, when precipitated in water from the reaction solution, the sulfonated poly(styrene) formed particles which could be easily separated by filtration. SPS_{20}, however, formed a suspension of quite small particles in water, although still separable by means of a filter paper. For this reason, we did not attempt to prepare polymers with higher degree of sulfonation.

Due to the remarkable conductivity, SPS_{20} is a potentially appealing membrane material for applications in various electrochemical systems and processes, also in view of its low cost as compared to Nafion. Particularly, we are interested in the development of novel ionomer membranes for use in electrochemical fuel cells operating at low temperature (60–90°C) with liquid methanol feed [23]. Possibly, such application requires that the membrane be proton conductive and impermeable to methanol at the same time [17,23]. This quality is best indicated by the ratio between hydrogen ion conductivity and methanol permeability, Φ; the higher this ratio, the better the membrane would perform in the fuel cell. The poly(styrene) utilized in this work is glassy at temperature below 87°C. When it is partially sulfonated, its glass

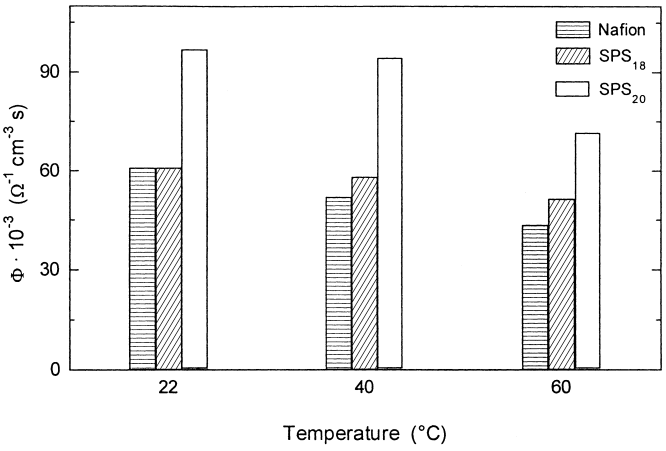

Fig. 6. Conductivity to permeability ratio, Φ, reported at various temperatures for two of the investigated membranes. The value relative to the Nafion 117 membrane was also measured and is reported for comparison.

transition temperature increases, according to the extent of sulfonation. The sulfonated polymer is generally glassy below around 100°C [24] and quite impermeable to methanol for sulfonation level up to 10 mol% at least. As already noted in Fig. 5, the permeability is considerably higher above 15 mol%. In Fig. 6 we report the conductivity to permeability ratio, Φ, for SPS_{18} and SPS_{20} membranes at temperature from 20°C to 60°C. The Nafion 117 membrane — which is at present most widely utilized in liquid-feed methanol fuel cells — is also included for comparison. It is worthy of note that Φ is higher for some of the SPS membranes than for Nafion. Also noted is that Φ improves as the poly(styrene) is increasingly sulfonated. The best result is obtained with SPS_{20}, which exhibits a conductivity to permeability ratio about 70% higher as compared to Nafion. This is attractive from the perspective of potential application in methanol fuel cell, because a decrease of methanol flux across the membrane – with proton conductance being unchanged – would be accompanied by a proportionate improvement of the cell efficiency and power density [23]. It would be important to assess the chemical stability of these membranes in a low temperature fuel cell with a liquid methanol feed. Although we did not observe any degradation of conductivity upon exposure of our SPS membranes to air or water at room temperature over a 2-months period, weak chemical resistance to peroxides and other active oxygen solutions was reported for various nonperfluorinated ionomers containing sulfonated poly(styrene) segments. Much greater stability in these chemical environments was found for a class of ionomers based on sulfonated poly(trifluorostyrene) [25,26]. The resistance to severe oxidizing solutions of the sulfonated poly(styrene) chains grafted to a poly(tetrafluoroethylene) backbone was substantially improved by substituting the tertiary hydrogen with methyl groups [27]. It has been proposed that oxidative species, particularly $HO_2^\bullet$ radicals, may occur in H_2/O_2 polymer electrolyte membrane fuel cells (PEMFC) as a result of direct combination on the anode surface of hydrogen and oxygen, the latter coming from the cathode compartment through the membrane [5,28]. The degradation of the membrane conductivity properties and of the fuel cell performance was ascribed to $HO_2^\bullet$ radicals, which cause cleavage of the sulfonated poly(styrene) segments [5,28]. According to this deterioration mechanism the life time of the above membrane materials in a H_2/O_2 PEMFC would be strongly dependent on the oxygen permeation rate through the membrane. In fact, although ionomer membranes containing poly(styrenesulfonic acid) segments deteriorated quickly in hydrogen peroxide solutions, they displayed considerable durability in a low temperature H_2/O_2 PEMFC [28]. If the above deterioration mechanism is correct and if $HO_2^\bullet$ radicals are actually produced by direct combination of hydrogen and oxygen at the anode, the stability of our SPS membranes might turn out to be acceptable in a DMFC, where no hydrogen is involved. However, direct experimental tests are necessary to address this issue unambiguously.

4. Concluding remarks

We prepared ion conductive materials based on sulfonated poly(styrene) (SPS) with a variety of density of the sulfonic acid groups. Membranes cast from some of these materials exhibited proton conductivity equal to that of Nafion membranes, which are largely used in electrochemical devices. In our preparations the sulfonate groups are directly attached to the phenyl ring of the base polymer. This procedure offers a number of important advantages as compared to other techniques which involve (radiation-induced) grafting of side chains onto the main polymer. SPS can be synthesized from relatively inexpensive materials according to our process. Since the reaction is carried out in a homogeneous liquid phase, the product is homogeneously sulfonated. Moreover, this procedure is proner than radiation-grafting to be implemented to a large-scale process. Such advantages would translate into a very low-cost of SPS as compared to Nafion and other grafted ionomers. Thus, SPS may be a valid option as a membrane material for a number of electrochemical uses. Of course, the chemical stability of SPS membranes has to be assessed with respect to the particular envisaged application.

Similarly to conductivity, the permeability to methanol also increases with the density of the sulfonate groups in the polymer. However, we found that even at the highest degree of sulfonation, the permeability of SPS is comparatively small: about 70% lower than that of Nafion membranes. That is

attractive particularly in relation to the methanol fuel cell technology. Application of SPS membranes to these electrochemical devices has the potential to improve their efficiency and power density. We emphasize, however, that we presently do not know the life time of these materials in a DMFC. Further research is necessary to address this issue.

Acknowledgements

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